DETECTION OF TRACE ELEMENTS IN SOLAR GRADE SILICON BY MASS SPECTROMETRY

M. Di Sabatino[1*], A. L. Dons[1], J. Hinrichs[2], O. Lohne[3], L. Arnberg[3]

[1] SINTEF, Materials and Chemistry, 7465 Trondheim (Norway)
[2] ThermoFisher Scientific Corporation, Advanced Mass Spectrometry, 28199 Bremen (Germany)
[3] Norwegian Univ. of Science and Technology (NTNU), Dep. of Materials Science and Eng., 7491 Trondheim (Norway)

ABSTRACT: The detection of trace elements in solar grade silicon plays a key role to assess and control the distribution of these elements in the final product, i.e., solar cells. In this study, we have used a recently developed Glow Discharge Mass Spectrometer (GD-MS) to measure the main doping elements, such as Al, B and P, as well as trace elements, such as Ca and Fe, in various multi crystalline silicon materials. The results show that GD-MS is a powerful tool that can detect the concentration of Al, B, P, Ca and Fe at level as low as ppb with good accuracy.
Keywords: SoG-silicon, Trace elements, Chemical analysis, Mass spectrometry

1 INTRODUCTION

The purity of solar grade silicon (SoG-Si), which is the purity required for producing solar cells, is approximately 99.99999% which means that the trace elements in PV materials is less than 1ppm (part per million). Therefore, there is a need for advanced instrumentation that can precisely assess the level of impurities in SoG-Si. Traditionally, trace elements analysis in high purity materials has been performed by many analytical techniques such as X-ray fluorescence-, atomic absorption-, optical emission- and infrared absorption spectroscopy [1]. In this study, the level of trace elements is detected by a mass spectrometer. The development of a new Glow Discharge Mass Spectrometer (GD-MS) by ThermoFisher Scientific [2] allows analyses of low detection limits, down parts per billion (ppb) in the solid, with a minimum of sample preparation effort. This work describes the procedures and results of GD-MS analyses in SoG-Si multi-crystalline materials.

1.1 Principle of the GD-MS

The instrument used in this study is a double-focussing high-resolution mass spectrometer which features a fast flow GD DC source using Argon carrier gas flows of about 400 ml/min. This is a high power source providing high sputter rates and sensitivity. The sputter rates for Al and Si matrices are on the order of 40 and 20 nm/s, respectively. The GD-MS detection system offers a wide linear dynamic range (0.2 cps to > 10^{12} cps). Figure 1 shows the main components of the GD-MS, namely: sample holder, plasma chamber, ion optic assembly, magnet, electro-static analyser, and detection system. The sample (approximately 20 mm diameter) acts as a cathode and a differential potential is created between the anode and the cathode in the plasma chamber. Due to the high electric field in the samples surface, Ar ions are accelerated towards the sample surface and different kind of ionization processes occur (Fig. 2). The sample ions, Sa^+, are then accelerated and focussed before entering the magnetic field. Due to the ratio M/z (mass of the element over its charge) the ions are separated by the analyzer. The intensity (counts per second, cps) of the element signal relative to the matrix signal allows quantification of the concentration of each element. The GD-MS manufacturer provides two kinds of sample holders: one for analysing flat sample geometries with diameters of 25-70 mm; the other allows the analysis of pin-shaped samples of 2-3 mm diameter and approximately 20 mm length.

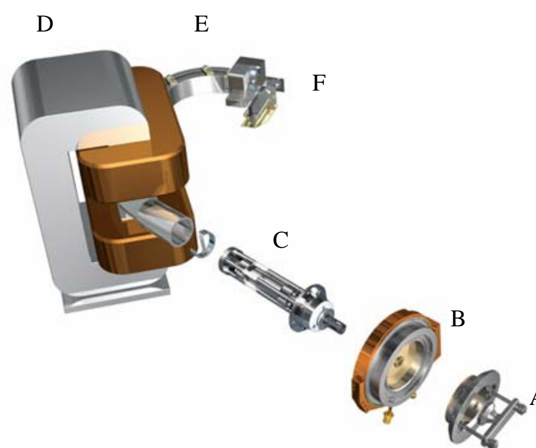

Figure 1: GD-MS main components: A - sample holder; B - plasma chamber; C - ion optic assembly; D - magnet; E - electro-static analyser; F - detector. (Courtesy ThermoFisher)

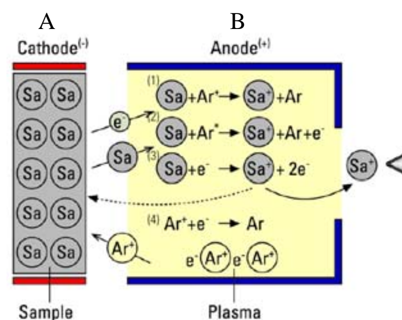

Figure 2: Schematic representation of A (sample) and B (plasma chamber) from Fig 1. Different types of ionization occur in the plasma chamber

2 EXPERIMENTAL

2.1 Casting procedure

The samples doped with Al, P, B, and Fe were cast in a directional solidification (DS) furnace, Crystalox

DC250 using solar grade silicon. More details of the furnace and casting process were previously given in ref. [3]. The ingots had a weight of 12 kg, a diameter of 250 mm and a height of 100 mm. The samples with the addition of Ca were industrially produced using metallurgical grade (MG) silicon (99.5wt%Si). Apart from the Fe doped ingot, three (Al doped ingot) to five (B and P) samples were cut at different heights of the ingot. Fe concentration at two different positions close to the bottom of the ingot was measured and compared with the values calculated from Scheil´s equation that takes into account the amount of doping elements added and their distribution coefficient. A list of the investigated samples is show in Table I.

Table I: List of the investigated samples

Sample	Description
A	Al doped by directional solidification
B	B doped by directional solidification
C	P doped by directional solidification
D	P doped by directional solidification + Fe addition
E	Industrial MG-Si + 0.1wt% Ca
F	Industrial MG-Si + 30wt% Ca

2.2 Sample preparation

Flat samples were taken from different positions along a multi crystalline (mc) silicon ingot as schematically shown in Fig. 3. The samples were ground with SiC papers (grid 180-320-500-1200) and cleaned.

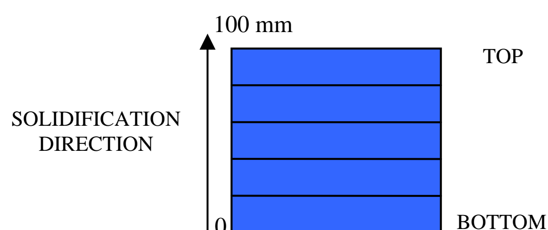

Figure 3: Schematic representation of the ingot and its solidification direction (the lines indicate the sample position)

Table II: Instrumental parameters

Parameter	Value
Discharge voltage	1100 V
Discharge current	60 mA
Discharge gas flow	300 ml/min
Focus lens	950 V

2.3 Tuning

Prior to the start of the sample analysis, the instrument was optimized for sensitivity and stability of the matrix signal. The discharge current, gas flow and voltage were adjusted in order to achieve the highest signal (on the order of 10^9-10^{10} cps) of the silicon matrix signal. Thereafter, the signal drift was observed over several minutes to make sure that stable discharge conditions could be maintained during the analysis period. Details of the instrument tuning parameters are shown in Table II.

2. 4 “Method”

Prior to analysing samples a “method” has to be developed. In the “method”, particularly the operator can choose:

- elements to be detected in the matrix
- isotopes
- scan/integration areas
- scan/integration times
- mass resolution

The correct choice of isotopes and resolutions is made by previous measurements of high purity and metallurgical grade samples using wide scan windows. The signals coming from elements or molecules with the same unit mass (e.g., ^{56}Fe and ^{40}Ar ^{16}O^{+}) will overlap and are often several orders of magnitude larger than the signal to be analysed. The resolution necessary for interference free analyses is used for the routine measurement. Whenever possible, the isotope of highest abundance must be used, providing the highest sensitivity and, thus, the lowest detection limits.

2.5 Sample analysis

We start the analysis by pre-sputtering the sample surface for 10 min and then the instrument starts the quantitative analysis of the elements selected in the method. Pre-sputtering is important in order to achieve stable discharge conditions and for surface contamination removal. Typically, each sample analysis takes approximately 5-10 min, depending on the method parameters, e.g. dimensions of the scan window and other parameters. For this investigation, we used 10 min pre-sputtering, 5 min integration time for each analysis and three analyses for each sample.

2.6 Calibration

The basic principle for quantitative analysis in GD-MS is the measurement of Ion Beam Ratios (IBR). The matrix element, for example Si, is directly measured and the trace metals normalised to the matrix ion beam. The certified concentrations of two MG-Si materials are plotted versus the measured IBRs of each element. The slope of the graph gives the relative sensitivity factors (RSFs) of the instrument.

In order to quantify the concentration of the selected element, the following equation for the selected elements in each sample was used:

$$C_{el} = IBR \cdot abundance_{el} \cdot RSF_{el}$$

where: C_{el} is the concentration of the element; IBR is the ratio of the intensities (cps) of the element and silicon; $abundance_{el}$ is the isotopic abundance of the isotope measured; RSF_{el} is the relative sensitivity factor for a given element which is applied from a Standard RSF table given by the instrument manufacturer [2].

Table III: Abundance and standard RSF values (measured for a steel matrix) for the selected elements (isotopes)

Element	Abundance (%)	Standard RSF
^{28}Si	92	1
^{11}B	80	2.13
^{31}P	100	1.20
^{27}Al	100	0.40
^{44}Ca	2	0.20
^{56}Fe	92	0.33

However, the Standard RSFs (Relative Sensitivity Factors) shown in Table III have been determined for a steel matrix and can therefore just semi-quantitatively be used for other matrices. In general, they tend to be accurate within a factor two for a silicon matrix.

In order to achieve the high dynamic range of 10^{12} cps, the instrument has three detector modes: (i) "Faraday" for high intensity of the matrix signal, (ii) "Analog" for medium intensity, and (iii) "Counting" for low intensity. These detector modes must be calibrated relative to each other in order to ensure correct calculation of the IBRs, and consequently the concentrations. The uncertainty in the RSFs and in the calibration makes it highly desirable to use standards of approximately the same composition as the specimen. The specimens in this work are going to be used as standard samples after we have compared the results with the resistivity measurements.

2.7 Resistivity measurements and Scheil´s equation

A four point probe [4, 5] method was used to measure the resistivity profiles along the ingots. This technique applies for both p-type (B or Al doping) and n-type (P doping) materials. The resistivity of a silicon ingot decreases as the level of dopant increases as shown in Fig. 4 [6].

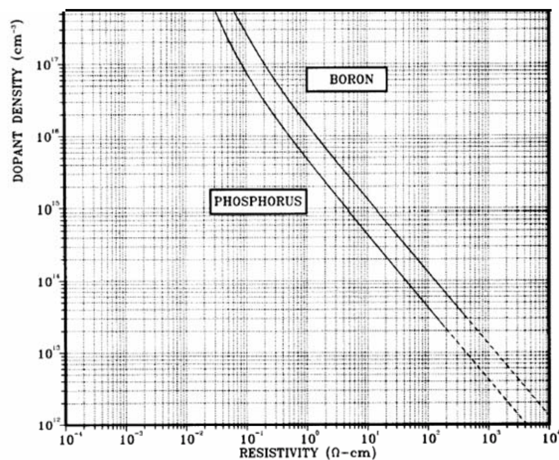

Figure 4: Relation between dopant level and resistivity. ASTM F23-99 [6]

The resistivity is nearly linear in the range 10^{-1}-10^{2} and the relationship may be written as:

$$\log R \approx -\log C + konst \qquad (1)$$

The resistivity measurements can be used to calculate the amount of doping element (as shown in Equation 1), and hence its distribution along the ingot.

The distribution of a doping element can be ideally calculated from the Scheil´s equation [7]:

$$C_s = k \cdot C_0 \cdot (1 - f_s)^{k-1} \qquad (2)$$

where: C_s is the concentration of the element in the solid matrix, C_0 is the initial concentration, k is the distribution coefficient, and f_s is the mass solid fraction.

As indicated by Equation 2, elements that have a distribution coefficient significantly less than one will present a high concentration at the top of the ingot and a very low concentration close to the bottom. The calculated values can be compared to the measurements given by the GD-MS. However, in this way it is possible to calculate only the concentration of the major doping elements (i.e., Al, B, P).

3 RESULTS and DISCUSSION

Figure 5 shows that Al concentration in a mc-Si ingot varies with the sputtering time. The measurements were started after GM-DS analysis of an Al matrix. After 15 min (10 min pre-sputtering + 5 min analysis) sputtering the Al concentration is 100 ppbw (weight) and after 20 min it decreases to approximately 50 ppbw. It further decreases to 40 ppbw after 25 min sputtering. The results reveal that there are some traces of Al in the instrument which affect the measurements. This effect is knows as "memory effect". Changing the extraction lens for each matrix will reduce this effect. Also, there might be some contaminations from grinding the sample surface. It is important to pre-sputter the sample surface in order to remove the effect of sample preparation, and use the same sputtering time when comparing the GMDS results of different samples. Moreover, it is necessary to have standard samples with roughly the same concentration of the elements contained in the investigated sample. Taking into account all these factors, absolute measurements can me achieved.

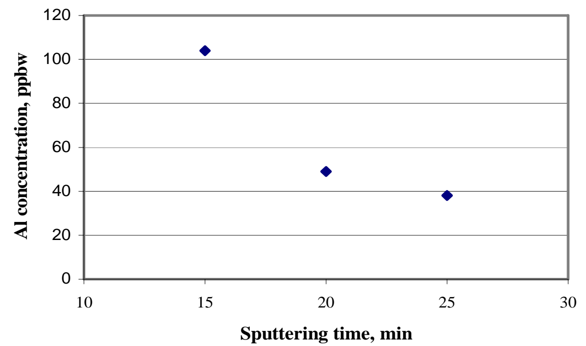

Figure 5: Three consecutive measurements of an Al doped mc-Si ingot after 15, 20, 25 min sputtering

The certified Ca concentrations of two MG-Si materials are plotted versus the measured IBRs, as shown in Fig. 6. This is a standard procedure for calibration. The slope of the graph gives the relative sensitivity factor (RSF) of Ca.

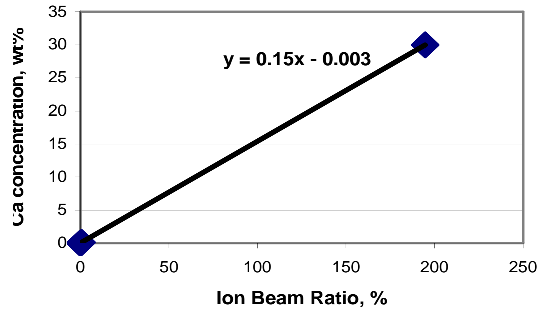

Figure 6: Calibration curve: calcium concentration (wt%) *vs* ion beam ratio for two different MG-Si materials

Table IV: Fe and Ca concentrations (ppbw) measured by GD-MS for the four alloys investigated

Sample	Fe	Ca
A	**1±0.3**	**4±1**
B	**2±0.5**	**1±0.3**
C	**5±1**	**1±0.3**
D	**7±2**	**3±1**

Table IV shows the Fe and Ca concentrations for the four alloys investigated (alloys A-D in Table I). The error bar is also shown. The GD-MS could measure concentrations as low as 1ppbw for both impurities.

The results of the GD-MS analysis show that the measurements are repeatable (approximately 90% reproducibility) and have good accuracy (25- 30%).

The results of the GD-MS measurements of the alloys A, B and C are shown in Fig.s 7-9. There is a good agreement between the chemical concentration of the main doping elements (Al, B and P, respectively) calculated by resistivity and the GD-MS measurements. All curves show similar trends. However, the chemical concentrations calculated by the resistivity measurements give slightly higher concentration values due to the contribution of other elements present in the silicon material which increases the resistivity values.

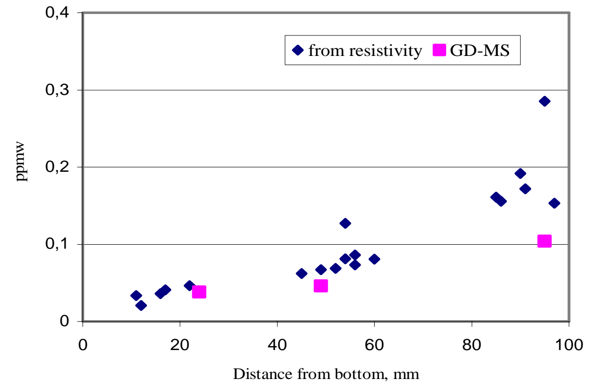

Figure 7: Al concentration (ppmw) vs distance from bottom (mm) (sample A)

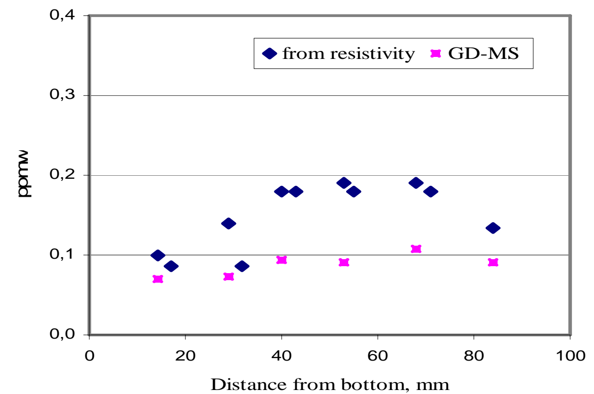

Figure 8: B concentration (ppmw) vs distance from bottom (mm) (sample B)

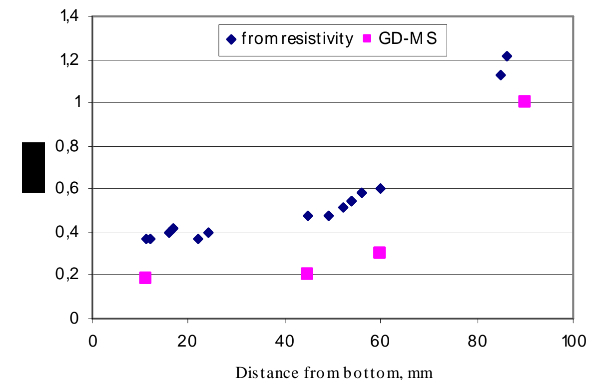

Figure 9: P concentration (ppmw) vs distance from bottom (mm) (sample C)

4 CONCLUDING REMARKS

This work has underlined that:

- GD-MS is a useful tool to measure the chemical composition of solar grade silicon. It can be used to measure elements at a level as low as a few ppbw. The instrument has good reproducibility (90%) and accuracy (25-30%).

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*Author for correspondence: M. Di Sabatino at SINTEF Materials and Chemistry - Marisa.di.sabatino@sintef.no